Acid Tartrate of 3-(1-Methyl-2-octahydroindolyl)-1-propanol (X). A hot solution of 0.77 g (5 mmoles) (+)-tartaric acid in 8 ml abs. ethanol was added to a solution of 1 g (5 mmoles) aminoalcohol V in 8 ml absolute ethanol. Cooling and partial evaporation gave tartrate X as a crystalline precipitate with mp 132-133°C (from abs. ethanol) in 64% yield. Found: C, 55.3; H 8.6; N, 4.0%. Calculated for $C_{16}H_{29}NO_7$: C, 55.3; H, 8.3; N, 4.0%.

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SATURATED NITROGEN-CONTAINING HETEROCYCLES.

12.* STRUCTURAL STUDIES OF CYCLOPENTA(b)PYRROLIDINYLALKANOLS

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^{13}C NMR spectroscopy and x-ray diffraction structural analysis were used to establish the stereochemistry of 3-[N-methyl-2-cyclopenta(b)pyrrolinyl]-1-propanol and its acetyl derivative. The absolute configuration was determined for 3-[N-methyl-2-cyclopenta(b)pyrrolidinyl]-1-propanol acid tartrate dihydrate and the conformational aspects of its cation and tartrate anion were studied.

The present communication is devoted to a study of the stereochemistry of the isomers of cyclopenta(b)pyrrolidinylalkanols obtained in the hydrogenation of furfurylcyclopentylamines in aqueous acid solutions [2] and in the catalytic hydroamination of furfurylidenecyclopentanone in acidic water—ethanol [3].

Gas-liquid chromatographic analysis indicated that both these reactions proceed with steric specificity and the cyclopentapyrrolidine alcohols I-III are formed, independently of their method of preparation and nature of the catalyst used, as one of the possible geometric isomers with 97% chromatographic purity. ^{13}C NMR spectroscopy, x-ray diffraction structural analysis

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*For Communication 11, see [1].

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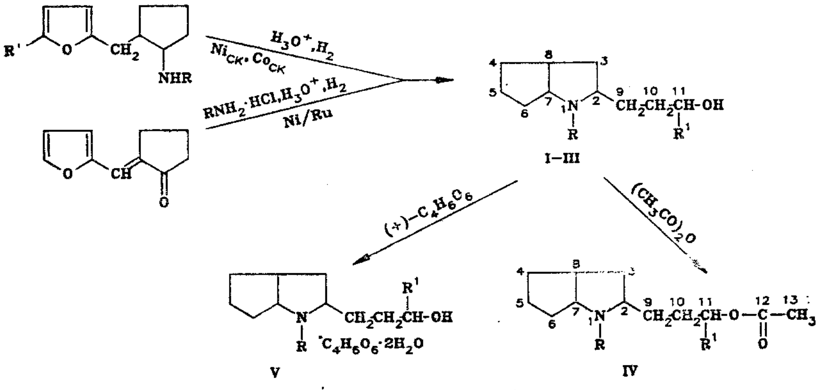
and comparison with the structure of isomeric pentalanes which are carbocyclic analogs were used to establish the structure of these heterocyclic compounds.



I R=R'=H; II,IV,V R=CH_3, R'=H; III R=R'=CH_3

$^{13}C\ \{^1H\}$ NMR spectroscopy was used for the complete assignment of the signals of aminoalcohol II and its acetyl derivative IV (Table 1). The methine, methylene, and methyl carbon atoms were distinguished using the off-resonance spectra. Considering the deshielding effect of the nitrogen atom and the strain of the condensed five-membered ring, the signals at 73.01, 39.38, and 66.00 ppm were assigned to the methine carbon atoms $C_{(7)}$, $C_{(8)}$, and $C_{(2)}$, respectively. The signal at 62.88 ppm was assigned to the carbon atom bearing the hydroxyl group, $C_{(11)}$, while the signal at 39.34 ppm was assigned to the methyl group carbon at nitrogen. The ^{13}C NMR spectra data for the cis and trans isomers of 3-(1-methyl-2-pyrrolidinyl)-1-propanol [4] permitted the establishment of the cis orientation of the hydrogen atoms at $C_{(2)}$ and $C_{(7)}$. The dependence of the chemical shift of the carbon atom containing the hydroxyl group on the molecular geometry was taken into account: This signal in the cis isomer is at 61-63 ppm, while it appears at 66-68 ppm in the trans isomer. The hydrogen atoms at $C_{(7)}$ and $C_{(8)}$ also occupy a cis position as indicated by the good agreement of the signals of angular $C_{(8)}$ in aminoalcohol II and substituted cis-pentalanes [5]. The signal for $C_{(11)}$ in 3-[1-methyl-2-cyclopenta(b)pyrrolidinyl]propyl-1-acetate (IV) is shifted downfield by 1.4 ppm due to the magnetic anisotropy of the acetyl group. The chemical shifts of the remaining carbon atoms correlate well with the signals for the analogous atoms in aminoalcohol II.

Thus, cis fusion for the carbocyclic and heterocyclic rings and cis,cis orientation of the hydrogen atoms at $C_{(2)}$, $C_{(7)}$, and $C_{(8)}$ were established for II.

In order to confirm the conclusions concerning the structure of cyclopentapyrrolidinylpropanol II on the basis of ^{13}C NMR spectroscopy and to elucidate the conformation of this compound, we carried out an x-ray diffraction structural study of the acid tartrate (V) obtained from this alcohol and (+)-tartaric acid. The geometry of the cation and anion of salt V is shown in Fig. 1. The atomic coordinates and their isotropic temperatre factors are given in Table 2. The bond and torsion angles are given in Tables 3 and 4, respectively.

The absolute configuration of the asymmetric carbon atoms of the cation was unequivocally determined on the basis of the known absolute configuration of the anion of (+)-tartaric acid. According to the Cahn–Ingold–Prelog nomenclature, the asymmetric centers at $C_{(2)}$, $C_{(7)}$, and $C_{(8)}$ in the cation have R, S, and S configuration, respectively.

Each of the cis-fused five-membered rings of the 2-azabicyclo[3.3.0]octane system has envelope conformation. The heterocycle has a greater departure from planarity than found for the carbocyclic analog. Thus, $C_{(2)}$ extrudes from the plane of the remaining atoms which is found with a precision of ±0.07 Å by 0.79(2) Å (the flexure along the $N \cdots C_{(3)}$ line is 50(1)°). On the other hand, the deviation of $C_{(6)}$ from the almost planar $C_{(5)}C_{(4)}C_{(8)}C_{(7)}$ system (which is planar to ±0.05 Å) is 0.39(2) Å and the flexure along the $C_{(5)} \cdots C_{(7)}$ line is 26.2(9)°.

The cis fusion of the five-membered rings results in the approximate orthogonality of their mean planes: the dihedral angle formed by the $C_{(7)}C_{(8)}C_{(3)}$ and $C_{(4)}C_{(5)}C_{(6)}C_{(7)}C_{(8)}$ planes is 75(1)°.

The bond lengths and angles in the anion and cation of salt V have ordinary values. A detailed consideration of these values is not worthwhile in view of the relatively high ex-

TABLE 1. ^{13}C NMR Spectra of Derivatives of Cyclopenta(b)pyrroline II and IV

Compound	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$	$C_{(8)}$	$C_{(9)}$	$C_{(10)}$	$C_{(11)}$	$C_{(12)}$	$C_{(13)}$
II	39,34	66,00	36,04	32,07	24,13	33,05	73,01	39,38	28,89	27,62	62,88	—	—
IV	38,94	66,63	38,94	32,59	24,09	33,69	72,79	39,52	29,12	24,97	64,27	169,18	20,36

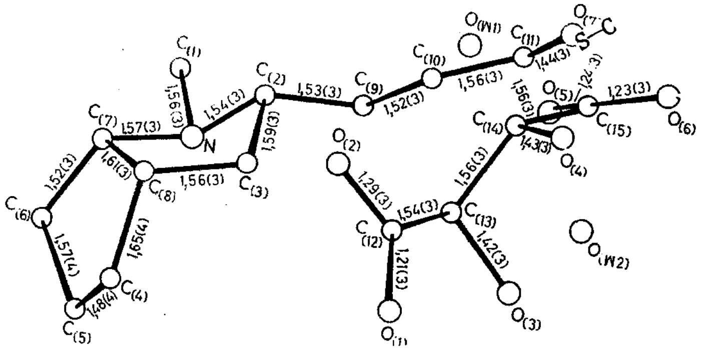


Fig. 1. Geometry of 3-[1-methyl-2-cyclopenta(b)pyrrolidinyl]-1-propanol acid tartrate dihydrate.

TABLE 2. Atomic Coordinates ($\cdot 10^3$) in V and Their Isotropic Temperature Factors

Atom	x	y	z	B_{iso}, Å²
$O_{(1)}$	179 (2)	812,4 (8)	857 (1)	3,6 (4)
$O_{(2)}$	183 (2)	895,4 (7)	740 (1)	3,1 (4)
$O_{(3)}$	−177 (2)	811,5 (7)	881 (1)	2,8 (3)
$O_{(4)}$	−119 (2)	795,3 (7)	631 (1)	2,8 (3)
$O_{(5)}$	−474 (2)	894,8 (7)	744 (1)	2,9 (3)
$O_{(6)}$	−474 (2)	807,6 (7)	634 (1)	3,0 (4)
$O_{(7)}$	140 (2)	919,5 (7)	400 (1)	3,2 (4)
$O_{(w1)}$	214 (2)	808,5 (7)	506 (1)	2,6 (3)
$O_{(w2)}$	−20 (2)	698,0 (7)	996 (1)	4,0 (4)
N	499 (2)	1128,0 (7)	701 (1)	2,0 (4)
$C_{(1)}$	370 (3)	1186 (1)	680 (2)	2,8 (5)
$C_{(2)}$	494 (3)	1084 (1)	597 (2)	1,8 (4)
$C_{(3)}$	663 (3)	1040 (1)	627 (2)	3,6 (6)
$C_{(4)}$	898 (4)	1067 (1)	790 (2)	4,8 (7)
$C_{(5)}$	824 (4)	1175 (1)	881 (2)	5,3 (7)
$C_{(6)}$	760 (3)	1170 (1)	821 (2)	2,9 (5)
$C_{(7)}$	702 (3)	1153 (1)	700 (2)	2,5 (5)
$C_{(8)}$	810 (3)	1089 (1)	667 (2)	3,3 (6)
$C_{(9)}$	311 (3)	1049 (1)	597 (2)	2,5 (5)
$C_{(10)}$	322 (3)	998 (1)	506 (2)	3,0 (5)
$C_{(11)}$	126 (3)	973 (1)	475 (2)	2,9 (5)
$C_{(12)}$	102 (3)	853 (1)	801 (2)	2,2 (5)
$C_{(13)}$	−106 (3)	861 (1)	811 (2)	1,9 (5)
$C_{(14)}$	−183 (3)	852 (1)	685 (2)	2,3 (5)
$C_{(15)}$	−397 (3)	850 (1)	686 (2)	1,7 (4)

perimental error. Unfortunately, the hydrogen atoms could not be localized in the structure of V (see Experimental). However, the intermolecular distances indicate that salt V has a branched system of hydrogen bonds (Table 5). The shortest intermolecular contact $O_{(2)}\cdots O_{(5)}$ is 2.51(2) Å apparently corresponds to a hydrogen bond involving the carboxyl hydrogen atom of the tartrate anion. In addition to the short $O_{(2)}\cdots O_{(5)}$ distance, this hypothesis is also supported by the difference between the lengths of the $C_{(12)}$–$O_{(1)}$ (1.21(3) Å), $C_{(15)}$–$O_{(6)}$ (1.23(3) Å), and $C_{(12)}$–$O_{(2)}$ (1.29(3) Å), $C_{(15)}$–$O_{(5)}$ (1.29(3) Å) bonds, which is common for such systems [6]. The anions are connected in infinite chains in the direction of the x-axis of the crystal due to hydrogen bonding. Due to the $\overset{+}{N}\cdots O_{(7)}$ hydrogen bonds [2.74(2) Å], the cations form spiral chains which extend in the direction of the 2_1 axis [00z]. Both systems of chains (the anionic and cationic chains) are linked to each other by hydrogen bonds involv-

TABLE 3. Bond Angles ω (deg) in the Structure of V

Bond angle	ω	Bond angle	ω
$\mathrm{C_{(1)}NC_{(2)}}$	109 (2)	$\mathrm{C_{(2)}C_{(9)}C_{(10)}}$	108 (2)
$\mathrm{C_{(1)}NC_{(7)}}$	107 (2)	$\mathrm{C_{(9)}C_{(10)}C_{(11)}}$	110 (2)
$\mathrm{C_{(2)}NC_{(7)}}$	103 (1)	$\mathrm{O_{(7)}C_{(11)}C_{(10)}}$	110 (2)
$\mathrm{NC_{(2)}C_{(3)}}$	99 (2)	$\mathrm{O_{(1)}C_{(12)}O_{(2)}}$	126 (2)
$\mathrm{NC_{(2)}C_{(9)}}$	109 (2)	$\mathrm{O_{(1)}C_{(12)}C_{(13)}}$	119 (2)
$\mathrm{C_{(3)}C_{(2)}C_{(9)}}$	114 (2)	$\mathrm{O_{(2)}C_{(12)}C_{(13)}}$	115 (2)
$\mathrm{C_{(2)}C_{(3)}C_{(8)}}$	102 (2)	$\mathrm{O_{(3)}C_{(13)}C_{(12)}}$	109 (2)
$\mathrm{C_{(5)}C_{(4)}C_{(8)}}$	109 (2)	$\mathrm{O_{(3)}C_{(13)}C_{(14)}}$	109 (2)
$\mathrm{C_{(4)}C_{(5)}C_{(6)}}$	106 (2)	$\mathrm{C_{(12)}C_{(13)}C_{(14)}}$	105 (2)
$\mathrm{C_{(5)}C_{(6)}C_{(7)}}$	108 (2)	$\mathrm{O_{(4)}C_{(14)}C_{(15)}}$	108 (2)
$\mathrm{NC_{(7)}C_{(6)}}$	109 (2)	$\mathrm{C_{(13)}C_{(14)}O_{(4)}}$	113 (2)
$\mathrm{NC_{(7)}C_{(8)}}$	100 (2)	$\mathrm{C_{(13)}C_{(14)}C_{(15)}}$	110 (2)
$\mathrm{C_{(6)}C_{(7)}C_{(8)}}$	107 (2)	$\mathrm{O_{(5)}C_{(15)}O_{(6)}}$	127 (2)
$\mathrm{C_{(3)}C_{(8)}C_{(4)}}$	110 (2)	$\mathrm{O_{(5)}C_{(15)}C_{(14)}}$	115 (2)
$\mathrm{C_{(3)}C_{(8)}C_{(7)}}$	108 (2)	$\mathrm{O_{(6)}C_{(15)}C_{(14)}}$	118 (2)
$\mathrm{C_{(4)}C_{(8)}C_{(7)}}$	103 (2)		

TABLE 4. Torsion Angles τ (deg) in Salt V

Angle	τ	Angle	τ
$\mathrm{O_{(7)}C_{(11)}C_{(10)}C_{(9)}}$	−172 (3)	$\mathrm{C_{(4)}C_{(8)}C_{(7)}N}$	−104 (3)
$\mathrm{C_{(11)}C_{(10)}C_{(9)}C_{(2)}}$	−162 (3)	$\mathrm{C_{(3)}C_{(8)}C_{(7)}N}$	12 (2)
$\mathrm{C_{(10)}C_{(9)}C_{(2)}N}$	−170 (3)	$\mathrm{C_{(3)}C_{(8)}C_{(7)}C_{(6)}}$	126 (3)
$\mathrm{C_{(10)}C_{(9)}C_{(2)}C_{(3)}}$	−61 (3)	$\mathrm{C_{(4)}C_{(8)}C_{(3)}C_{(2)}}$	103 (2)
$\mathrm{C_{(3)}C_{(2)}NC_{(1)}}$	168 (3)	$\mathrm{C_{(7)}C_{(8)}C_{(3)}C_{(2)}}$	19 (2)
$\mathrm{C_{(9)}C_{(2)}NC_{(1)}}$	−73 (2)	$\mathrm{C_{(8)}C_{(3)}C_{(2)}N}$	−44 (2)
$\mathrm{C_{(3)}C_{(2)}NC_{(7)}}$	54 (2)	$\mathrm{C_{(8)}C_{(3)}C_{(2)}C_{(9)}}$	−159 (3)
$\mathrm{C_{(9)}C_{(2)}NC_{(7)}}$	173 (3)	$\mathrm{O_{(1)}C_{(12)}C_{(13)}O_{(3)}}$	−6 (2)
$\mathrm{C_{(1)}NC_{(7)}C_{(6)}}$	92 (3)	$\mathrm{O_{(1)}C_{(12)}C_{(13)}C_{(14)}}$	−123 (3)
$\mathrm{C_{(1)}NC_{(7)}C_{(8)}}$	−156 (3)	$\mathrm{O_{(2)}C_{(12)}C_{(13)}O_{(3)}}$	−179 (3)
$\mathrm{C_{(2)}NC_{(7)}C_{(8)}}$	−41 (2)	$\mathrm{O_{(2)}C_{(12)}C_{(13)}C_{(14)}}$	65 (3)
$\mathrm{C_{(2)}NC_{(7)}C_{(6)}}$	−152 (2)	$\mathrm{O_{(3)}C_{(13)}C_{(14)}O_{(4)}}$	−65 (2)
$\mathrm{NC_{(7)}C_{(6)}C_{(5)}}$	84 (2)	$\mathrm{O_{(3)}C_{(13)}C_{(14)}C_{(15)}}$	56 (2)
$\mathrm{C_{(8)}C_{(7)}C_{(6)}C_{(5)}}$	−24 (3)	$\mathrm{C_{(12)}C_{(13)}C_{(14)}O_{(4)}}$	51 (2)
$\mathrm{C_{(7)}C_{(6)}C_{(5)}C_{(4)}}$	30 (3)	$\mathrm{C_{(12)}C_{(13)}C_{(14)}C_{(15)}}$	173 (3)
$\mathrm{C_{(6)}C_{(5)}C_{(4)}C_{(8)}}$	−22 (2)	$\mathrm{O_{(4)}C_{(14)}C_{(15)}O_{(5)}}$	173 (3)
$\mathrm{C_{(5)}C_{(4)}C_{(8)}C_{(3)}}$	−106 (3)	$\mathrm{O_{(4)}C_{(14)}C_{(15)}O_{(6)}}$	−7 (2)
$\mathrm{C_{(5)}C_{(4)}C_{(8)}C_{(7)}}$	8 (2)	$\mathrm{C_{(13)}C_{(14)}C_{(15)}O_{(5)}}$	48 (2)
$\mathrm{C_{(4)}C_{(8)}C_{(7)}C_{(6)}}$	10 (2)	$\mathrm{C_{(13)}C_{(14)}C_{(15)}O_{(6)}}$	−131 (2)

ing the two water solvate molecules, one of which forms four hydrogen bonds, while the other forms three hydrogen bonds.

Thus, the results of the x-ray diffraction structural study of tartrate V confirm our previous conclusions relating to the structure of aminoalcohol II.

EXPERIMENTAL

At 20°C, the crystals of V are orthorhombic with $a = 7.295(1)$, $b = 21.115(4)$, $c = 11.762(1)$ Å, $d_{calc} = 1.17$ g/cm^3, $Z = 4$, space group $P2_12_12_1$. The unit cell parameters and reflections of 662 independent reflections with $F^2 > 3\sigma$ were measured on a Hilger-Watts Y/200 four-circle automatic diffractometer at 20°C using $\lambda \mathrm{MoK}_\alpha$ radiation, graphite monochromator, $\theta/2\theta$ scan, $\theta \leq 30°$. The structure was deciphered by the direct method usingthe MULTAN program and refined in the full-matrix method of least squares in the isotropic approximation to $R = 0.109$ ($R_\omega = 0.105$). The hydrogen atoms were not found. All the calculations were carried out on an Eclipse S/200 minicomputer using the INEXTL programs [7].

The ^{13}C NMR spectra were taken on a Varian FT-80A spectrometer at 20 MHz for $CDCl_3$ solutions at 35°C. The spectra were calibrated relative to the solvent signal; the middle peak is at 76.9 ppm from TMS.

The gas-liquid chromatography was carried out on an LKhM-8MD chromatograph under conditions described in our previous work [1]. The retention time for aminoalcohol obtained by different procedures was 3.85 min on the column packed with 10% SE-30 and 6.30 min on the column packed with 15% Apiezon L.

TABLE 5. Possible Hydrogen Bonds in the Crystal Structure of V (d is the length of hydrogen bond)

Bond	d, Å
$O_{(2)}(-1+x, y, z) \cdots O_{(5)}(x, y, z)$	2,51 (2)
$\overset{+}{N}_{(x, y, z)} \cdots O_{(7)}(0{,}5-x, 2-y, -0.5+z)$	2,74 (2)
$O_{(w1)} \cdots O_{(4)}(x, y, z)$	2,85 (2)
$O_{(w1)} \cdots O_{(4)}(0{,}5+x, 1{,}5-y, 1-z)$	2,99 (2)
$O_{(w1)} \cdots O_{(6)}(1+x, y, z)$	2,73 (2)
$O_{(w1)} \cdots O_{(7)}(x, y, z)$	2,71 (2)
$O_{(w2)} \cdots O_{(1)}(-0{,}5+x, 1{,}5-y, 2-z)$	2,80 (2)
$O_{(w2)} \cdots O_{(3)}(x, y, z)$	2,98 (2)
$O_{(w2)} \cdots O_{(3)}(0{,}5+x, 1{,}5-y, 2-z)$	2,90 (2)

Compounds I-IV were prepared according to our previous work [2, 3].

3-[1-Methyl-2-cyclopenta(b)pyrrolidinyl]-1-propanol Acid Tartrate Dihydrate. A hot solution of 0.77 g (5 mmoles) (+)-tartaric acid in 8 ml ethanol (45-50°C) was added to a solution of 0.945 g (5 mmoles) aminoalcohol II in 8 ml ethanol. Cooling to room temperature and evaporation of two-thirds of the volume gave a crystalline precipitate of tartrate dihydrate V, mp 97-99°C (from ethanol) in 85% yield. Found: C, 50.0; H 8.5; N 4.1%. Calculated for $C_{15}H_{30}NO_9$: C 50.0; H 8.3; N 3.9%.

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